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ABSTRACT

BIOMIMETIC STRATEGY FOR CARBON DIOXIDE CAPTURE

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INTRODUCTION

Carbon dioxide (CO₂) control is crucial for all missions. Cabin air CO₂ is about 10-times ambient. Yet, increases in pCO₂ above Earth-ambient of only 2.7-fold result in “stuffy” feelings. The 180-day SMAC is 19 times Earth-ambient and, at 29 times increase one reaches the upper limit of normal operations. Long duration missions, e.g., to Mars, need a new generation CO₂ capture technology that is light, small, efficient, stable and requires little energy or maintenance, while attaining a CO₂ level as close to Earth ambient as possible. We have looked beyond current physicochemical absorbent and adsorbent technologies to engineer a stable biomimetic reactor modeled after the vascular and pulmonary systems.

CURRENT STATUS OF RESEARCH

Methods

The enzyme carbonic anhydrase (CA, E.C. 4.2.1.1) in several discrete forms is responsible for extraction of CO₂ from tissues and its transport in the vascular system, as bicarbonate, followed by the removal of CO₂ from the vasculature to the air at the lung. We created a contained liquid membrane (CLM) enriched in CA and retained by microporous polypropylene. In our experiments the one side (feed) of the CLM contacted an air-CO₂ mixture at a total pressure of 101.3 kPa with CO₂ concentrations ranging from 400 ppm to 100,000 ppm at temperatures ranging from 20° to 40° and with relative humidity ranging from 4% to 75%. The other side (permeate or sweep side) of the CLM contacted either an argon sweep gas at 101.3 kPa and relative humidity 0% or a vacuum (≈ kPa). Chemical characteristics of the CLM were: pH – 6.5 to 8, phosphate buffer 10 to 100 mM, CA concentration – 16 μM to 156 μM.

The gas stream was analyzed continuously by means of a residual gas analyzer mass spectrometer with a sensitivity of 10 ppm. Each graph point is the average of three data recordings. When relevant the standard deviation is displayed.

Results

A comparison of the mass transfer resistance of the polymer retaining film and the liquid membrane (with and without CA) showed that for CO₂ the polymer membrane presents relatively little resistance as compared to the liquid, but becomes increasingly relevant with increased CA activity. Specifically, the ratio of the mass transfer resistance presented by the microporous polymer to that of the buffer liquid (without CA) was 1:1350. However, in the presence of 33.3 μM CA, the ratio of polymer to liquid membrane resistance dropped to 1:250. The resistance ratio of the aqueous buffer, with and without CA, was 1:5.5.

CLM parameter optimization revealed the following: CA concentration of 100 to 133 μM yields a CO₂ permeance at a feed concentration of 1,000 ppm of $5.6 \cdot 10^{-8}$ moles m⁻² Pa⁻¹ s⁻¹ with selectivity against oxygen (O₂) of 631:1 and against nitrogen (N₂) of 882:1. Under conditions of CA at 33.3 μM and membrane at 133 μm the optimal buffer concentration is 50 mM. Under these conditions the preferred pH of the reactor is 8. This indicates a need to drive the reaction towards hydration given the significant driving force for CO₂ removal at the permeate side. Further studies done over a range of CLM thickness (75 μm to 175 μm) revealed that CO₂ permeance declined rapidly from a CLM thickness of 75 μm to 133 μm and then more slowly beginning at 133 to 175 μm. In contrast, the selectivity

increased linearly as a function of thickness. These results indicate the need to investigate the use of facilitated diffusion in order to get high permeance at a thickness that will provide high selectivity.

For a given concentration of enzyme CO₂ permeance is a function of partial pressure as it interacts with the number of enzyme molecules available for catalysis. At pCO₂ of 400 ppm permeance is about 3×10^{-8} moles m⁻² Pa⁻¹ s⁻¹ but selectivity is maximal. At pCO₂ of 10,000 ppm permeance increases to 1×10^{-7} moles m⁻² Pa⁻¹ s⁻¹. Temperature optima increase non-linearly with the maximal rate of increase at temperatures in excess of 35°. At 40° permeance is 1.5-fold higher than at 20°. Permeance in this reactor design is independent of humidity over the entire range tested. The membrane remained stable over a test period of 30 h.

Conclusion

We examined the operational profile of an enzyme-based CO₂ capture CLM reactor in parametric studies. The data show that it functions extremely well and is stable for considerable duration. It could run in either sweep or vacuum mode. At this time the resistance of the polymer retaining film is negligible though it will become greater with future improvements in CO₂ permeance. It gives a direction to future studies. With increased thickness this number declines favoring non-catalyzed transport. This observation also indicates future directions of import.

Compared with other non-enzymatic CLM designs the separation index (selectivity x permeance) is 2.9-fold better. Compared with polymer membranes alone the performance is 237 times better. In addition, the enzyme-based bioreactor CLM membrane requires significantly less energy than polymer membranes, molecular sieve or metal oxides.

FUTURE PLANS

These data point to several investigations needed to move to development and simulation testing, as in Bio-Plex. These include additional vacuum studies, use of heterogeneous catalyst to increase interfacial contact efficiency and use of electrodiffusion to allow thicker membranes to increase selectivity. In addition we will test using an ersatz atmosphere to control for cabin VOCs.

INDEX TERMS

Carbon dioxide, CO₂, ARS, carbonic anhydrase, enzyme, biomimetic, CO₂ capture, ALS, membrane